(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 069 500**
B1

(12) # EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **02.01.86**

(51) Int. Cl.⁴: **C 08 K 5/00**, C 09 K 21/10, C 09 K 21/12

(21) Application number: **82303224.8**

(22) Date of filing: **21.06.82**

(54) **Intumescent flame retardant compositions.**

(30) Priority: **06.07.81 US 280569**

(43) Date of publication of application:
12.01.83 Bulletin 83/02

(45) Publication of the grant of the patent:
02.01.86 Bulletin 86/01

(84) Designated Contracting States:
DE FR GB IT

(56) References cited:
EP-A-0 025 082
US-A-3 873 496

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EP 0 069 500 B1

Courier Press, Leamington Spa, England.

Description

This invention relates to intumescent compositions and more particularly to intumescent compositions comprising a bicyclic phosphate compound and a compound of nitrogen. The intumescent compositions of this invention impart flame retardant and intumescent character to polymers.

Intumescent compositions may be generally described as those compounds and mixtures which swell upon heating to produce a voluminous char or residue. A familiar example of such compositions is mercuric thiocyanate or "pharaoh's serpents" which, when ignited, forms a voluminous ash that resembles a moving serpent. Other compositions have been formulated which combust to form adherent, tough insulating foams that resist further burning and act to insulate and protect the underlying substrate. These formulations have found wide commercial use in fire retardant paints and mastics.

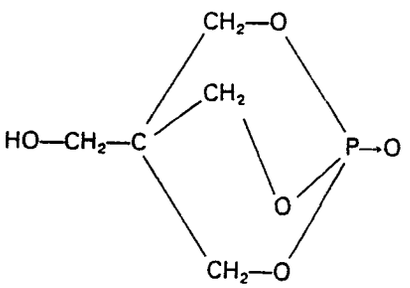
More recently, additives have been incorporated into molding resins which render them intumescent and flame retardant. In U.S. patents 3,936,416 and 4,201,705 there are described polyolefin compositions containing melammonium polyphosphates and phosphate esters which are flame retarded. Upon combustion, a tough, insulating char forms at the surface of the molded article which resists further burning and acts to protect the bulk of the polyolefin resin from further burning.

As is well known in the art, the behavior of flame retardant additives in resin formulations varies greatly with the nature of polymeric substrate. This is particularly true with intumescent compositions since the rapid formation of the protective char layer is highly dependent upon such factors as the combustion temperature and the viscosity of the melt formed by the burning substrate. Other considerations that may also come into play even where the intumescent behavior is optimum include the effect of the additive on the physical properties, color and molding characteristics of the base resin. The development of intumescent additives for use in flame retarding resins thus remains a highly empirical art wherein predictability of behavior is rare to non-existent, and the art has largely concentrated on the development of highly specific additive combinations for particular resins and end-uses.

The development of an intumescent additive combination which exhibits a greater latitude in dispersability and char-forming character and thus capable of being formulated for use in a wider variety of dissimilar resins would thus be a useful advance in the flame retardant art.

The present invention provides a composition suitable for addition to a polymeric resin to impart intumescence thereto, comprising 2,6,7 - trioxa - 1 - phosphobicyclo[2.2.2]octane - 4 - methanol - 1 - oxide (PEPA), and a nitrogen compound which is a melamine, ammeline, cyanuric acid, benzoguanamine, cyanamide, an urea or a guanidine or a salt thereof or an ammonium salt. The composition may be used to impart a degree of flame retardant and intumescent character to various resins, namely polyolefins, polyvinyl-aromatic resins, polycarbonate resins, polyacrylate resins, polyamides, polyvinyl chloride and blends thereof.

The bicyclic phosphate compound, PEPA, which may be represented by the formula:



is a known phosphate compound and may readily be prepared by conventional processes as described in US—A—3,293,327. PEPA has been disclosed for use as flame retardant in polyesters and particularly in polyester fibers as described in US—A—3,873,496, however PEPA alone is not an intumescent additive for polyesters and is described in US—A—3873496 as a thermally stable flame retardant and unreactive with molten polyesters.

The bicyclic phosphate compound PEPA is used with the nitrogen compound to provide an intumescent composition. Ammonium salts which can be used as the nitrogen compound are ammonium phosphate and ammonium polyphosphate.

The intumescent compositions of this invention comprise mixtures of from 5 to 95 wt.% PEPA and from 95—5 wt.% of the nitrogen compound. The specific ratio employed will depend in part upon the particular nitrogen compound employed, in as much as the various nitrogen compounds are not equally effective in producing intumescent behavior.

The intumescent compositions of this invention, when further compounded with a polymeric resin will impart flame retardant and intumescent character. Polymers which exhibit intumescent behavior when compounded with a sufficient amount of an intumescent composition of this invention are polyolefins, polyvinylaromatic resins such as polystyrene, styrene-acrylonitrile copolymers and ABS graft copolymers,

polycarbonate resins such as bisphenol-A polycarbonate, polyacrylate resins such as polymethyl methacrylate, polyamides such as Nylon 6, and polyvinylchloride, as well as blends and alloys of these resins. As would be expected, not every intumescent combination of PEPA and nitrogen compound is effective in producing a desirable level of intumescence in every polymeric resin, and one skilled in the art will recognize the need for evaluating and selecting particular combinations for particular end uses. In general when employed at levels above 20 parts by weight of intumescent composition per hundred parts by weight of resin, intumescent characteristics will be present. The degree of intumescence will increase with increased levels of intumescent additive compositions, and for some purposes, the including of as much as 60 parts by weight of intumescent composition per hundred parts by weight of resin may be preferred.

The compounding of the polymer with the intumescent composition may be accomplished by any of the conventional compounding processes including powder blending, Banbury mixing and melt extrusion. Those skilled in the art will recognize that the particular intumescent composition selected for use with a particular resin will necessarily be stable at the processing temperature when melt processing is to be carried out. Where it is desired to use compositions which decompose at or near the melt temperature of the resin, powder blending and compression molding may be employed to minimize premature decomposition and intumescing.

The preparation of the intumescent compositions of this invention and the use of such compositions in flame retardant resins will be better understood by consideration of the following Examples.

The Limiting Oxygen Index (LOI) test is employed to determine the minimum concentration of oxygen, in percent, which will support combustion of a test sample. The test is more fully described in ASTM-D-2863-70.

The UL-94 flame test is a standard test for rating the vertical burn characteristics of a test sample.

Examples 1—15

In the following Examples, 1:1 mixtures of PEPA and the indicated nitrogen compound were prepared by simple mixing of the powdered and/or liquid compounds. The mixtures were tested for intumescent behavior by placing a sample on the tip of a laboratory spoon and exposing the sample to a bunsen burner flame for 5 to 10 sec. The compositions of the mixtures and their respective intumescent behavior are summarized in Table I.

TABLE I
Intumescent character of 1:1 PEPA/nitrogen compound mixtures

Example No.	Nitrogen compound	Intumescent behavior
1	Melamine	+
2	Melamine, Acetic Acid Salt	+
3	Melamine HBr	+
4	Bis-melammonium pentate[1]	+
5	Melamine-formaldehyde resin	+
6	Benzoguanamine	+
7	Benzoguanamine phosphate	+
8	Ammeline	+
9	Cyanuric Acid	+
10	Ammonium polyphosphate	+
11	Cyanamide	+
12	Urea	+
13	Guanidine HCl	+
14	Cyanoguanidine	+
15	Thiourea	+

Notes: [1] dipentaerythritol diphosphate salt of melamine; see U.S. 4,154,930

It will be apparent that mixtures of PEPA with a variety of nitrogen compounds are intumescent.

Examples 16—36

In the following Examples (in which Examples 34 to 36 are controls), compositions containing PEPA:Nitrogen Compound:Resin in a ratio of 1:1:1 were similarly prepared by simple mixing of the powdered resin with the PEPA/nitrogen composition. Testing for intumescent behavior was again accomplished by placing a sample on the tip of a laboratory spoon and holding the sample on a bunsen burner flame for 5—10 sec. The compositions and intumescent behavior of these mixtures are summarized in Table II.

TABLE II

Intumescent behavior of PEPA/nitrogen compound/resin (1:1:1) blends

Example No.	Nitrogen compound	Resin[1]	Intumescent[2] behavior
16	Melamine	ABS	+
17	Melamine	SAN	Slight
18	Melamine	Polycarbonate	+
19	Melamine	PVC	+
20	Melamine	PP	+
21	Melamine	PE	+
22	Ammonium Polyphosphate	ABS	+
23	"	SAN	Slight
24	"	Polycarbonate	+
25	"	PVC	+
26	"	PP	+
27	"	PE	+
28	Guanidine	ABS	+
29	"	SAN	+
30	"	Polycarbonate	+
31	"	PVC	+
32	"	PP	+
33	"	PE	+
34 (control)	Glycine	ABS	V. Slight
35 (control)	"	PP	Slight
36 (control)	"	PE	Slight

Notes

[1]ABS=Styrene-Acrylonitrile-butadiene graft copolymer; SAN=Styrene-Acrylonitrile copolymer; Polycarbonate=bisphenol-A polycarbonate resin; PVC=polyvinyl chloride; PP=polypropylene; PE=polyethylene.

[2]+=substantial char remains after burning; slight=only slight amount of char formation.

The variation of char forming character with resin type and nitrogen compound will be apparent from these data. Although PEPA/melamine and PEPA/ammonium polyphosphate mixtures are effective char formers in a variety of resins including polypropylene (Examples 20 and 26) and PVC (Examples 19 and 25), the same combinations produced only slight char formation in SAN (Examples 17 and 23). A mixture of PEPA and guanidine, however, was an effective char former in SAN (Example 29). However, a PEPA/glycine mixture, in itself an effective intumescent was only slightly effective as a char-former when compounded with resins at this level (Examples 34—36).

Examples 37—49

In the following Examples, the flame retardant behavior of representative resin compositions containing mixtures of PEPA and nitrogen compounds as intumescent additives at various levels was measured by the UL-94 and LOI methods. The resin compositions were prepared by compounding the indicated resin in the mixing head of a Brabender extruder, then extruding the composition. The resin composition was then chopped and compression molded to form specimens for testing. The compositions and the UL-94 and LOI test results are summarized in Table III.

TABLE III

PEPA/nitrogen compound as flame retardants

Example No.	N-compound	P/N[1] ratio	Resin[2]	Loading[3] phr	UL94 test	LOI	Intumescent
37	Melamine	2.9/1	PP	30	V-O	29.3	+
38	"	3.6/1	PP	30	V-O	31.5	+
39	"	4/1	PP	22	V-0	31.1	+
40	"	4/1	PP	20	V-1	30.1	+
41	"	4/1	Nylon 6	26	V-0	27.5	+
42	Melamine Phosphate	1.6/1	PP	20	V-0	29.8	+
43	"	1.5/1	Styrene	50	V-0	29.7	+
44	"	.8/1	"	45	NVE	22.3	V. Light
45	Ammonium Polyphosphate	1.5/1	PP	30	V-0	29.5	+
46	Benzoguanamine Phosphate	1.5/1	PP	30	V-2	26.8	+
47	Melamine Cyanurate	1.7/1	PP	30	NVE	30.6	+
48	Melamine Phosphate	1.5/1	PMMA	50	V-0	36.5	+
49	"	1/1	ABS/Nylon	27.7	V-0	29.6	+

Notes

[1]P/N ratio=weight ratio of PEPA to nitrogen compound

[2]PP=polypropylene; ABS/Nylon=100 pbw ABS, 30 pbw Nylon 6 alloy

[3]Loading=parts by weight of PEPA/N compound per hundred parts resin

The ability of the intumescent compositions of this invention to impart intumescent and flame retardant character to resins is apparent from these data. Not all compositions produce flame retardant V-0 character to all resins. Thus, although compositions of Examples 40, 44, 46 and 47 exhibit intumescence and high LOI values, these resins were not rendered V-0. As will be apparent from a comparison of Examples 43 and 44, intumescent and flame retardant character is affected by the ratio of PEPA to nitrogen compound. Although some intumescent behavior will be seen in resins at some loading level for all P/N ratios, generally ratios of 1:1 and greater will be preferred.

The invention will thus be seen to be intumescent compositions comprising PEPA and a nitrogen compound which may be adapted to render polymeric resins intumescent and flame retardant.

Claims

1. An intumescent composition comprising a resin selected from polyolefins, polyvinylaromatic resins,

polycarbonate resins, polyacrylate resins, polyamides, polyvinyl chloride and blends thereof; 2,6,7 - trioxa - 1 - phosphobicyclo[2.2.2]octane - 4 - methanol - 1 - oxide; and a nitrogen compound which is a melamine, ammeline, cyanuric acid, benzoguanamine cyanamide, an urea or a guanidine or a salt thereof, or an ammonium salt.

2. An intumescent composition according to claim 1 comprising from 5 to 95 wt.%, based on the total weight of the 2,6,7 - trioxa - 1 - phosphobicyclo[2.2.2]octane - 4 - methanol - 1 - oxide and the nitrogen compound, of the 2,6,7 - trioxa - 1 - phosphobicyclo[2.2.2]octane - 4 - methanol - 1 - oxide and from 95 to 5 wt.%, based on the total weight of the 2,6,7 - trioxa - 1 - phosphobicyclo[2.2.2]octane - 4 - methanol - 1 - oxide and the nitrogen compound, of the nitrogen compound.

3. Shaped articles prepared from an intumescent composition as claimed in claim 1 or 2.

4. A composition, suitable for addition to a polymeric resin to impart intumescence thereto, comprising 2,6,7 - trioxa - 1 - phosphobicyclo[2.2.2]octane - 4 - methanol - 1 - oxide, and a nitrogen compound which is a melamine, ammeline, cyanuric acid, benzoguanamine, cyanamide, an urea or a guanidine or a salt thereof or an ammonium salt.

5. A composition according to claim 4 comprising from 5 to 95 wt.%, based on the total weight of the 2,6,7 - trioxa - 1 - phosphobicyclo[2.2.2]octane - 4 - methanol - 1 - oxide and the nitrogen compound, of the 2,6,7 - trioxa - 1 - phosphobicyclo[2.2.2]octane - 4 - methanol - 1 - oxide and from 95 to 5 wt.%, based on the total weight of the 2,6,7 - trioxa - 1 - phosphobicyclo[2.2.2]octane - 4 - methanol - 1 - oxide and the nitrogen compound, of the nitrogen compound.

Patentansprüche

1. Intumeszierende Zusammensetzung bestehend aus einem Harz, ausgewählt aus der Gruppe Polyolefine, polyvinylaromatische Harze; Polycarbonatharze, Polyacrylatharze, Polyamide, Polyvinylchlorid und Gemische davon; 2,6,7 - Trioxa - 1 - phosphobicyclo - [2.2.2] - octan - 4 - methanol - 1 - oxid; und eine Stickstoffverbindung, die ein Melamin, Ammelin, Cyanursäure, Benzoguanamin, Cyanamid, ein Harnstoff oder ein Guanidin oder ein Salz davon oder ein Ammoniumsalz ist.

2. Intumeszierende Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß sie, bezogen auf das Gesamtgewicht von dem 2,6,7 - Trioxa - 1 - phosphobicyclo - [2.2.2] - octan - 4 - methanol - 1 - oxid und der Stickstossverbindung, 5 bis 95 Gew.-% des 2,6,7 - Trioxa - 1 - phosphobicyclo - [2.2.2] - octan - 4 - methanol - 1 - oxids und 95 bis 5 Gew.-% der Stickstoffverbindung enthält.

3. Geformte Gegenstände, hergestellt aus einer intumeszierenden Zusammensetzung nach einem der Ansprüche 1 und 2.

4. Zusammensetzung, die als Zusatz zu einem polymeren Harz geeignet ist um ihm Intumeszenz zu verleihen, bestehend aus 2,6,7 - Trioxa - 1 - phosphobicyclo - [2.2.2] - octan - 4 - methanol - 1 - oxid und einer Stickstoffverbindung, die ein Melamin, Ammelin, Cyanursäure, Benzoguanamin, Cyanamid, ein Harnstoff oder ein Guanidin oder ein Salz davon oder ein Ammoniumsalz ist.

5. Zusammensetzung nach Anspruch 4, dadurch gekennzeichnet, daß sie, bezogen auf das Gesamtgewicht von den 2,6,7 - Trioxa - 1 - phosphobicyclo - [2.2.2] - octan - 4 - methanol - 1 - oxid und der Stickstoffverbindung, aus 5 bis 95 Gew.-% des 2,6,7 - Trioxa - 1 - phosphobicyclo - [2.2.2] - octan - 4 - methanol - 1 - oxids und 95 bis 5 Gew.-% der Stickstoffverbindung besteht.

Revendications

1. Composition intumescente comprenant une résine choisie parmi les polyoléfines, résines polyvinyl aromatiques, résines polycarbonate, résines polyacrylate, polyamides, chlorure de polyvinyle et leurs mélanges; du trioxa - 2,6,7 - phospho - 1 - bicyclo[2.2.2]octane méthanol-4 oxyde-1; et un composé azoté qui est une mélane, amméline, acide cyanurique, benzoguanamine, cyanamide, une urée ou une quanidine ou un de leurs sels, ou un sel d'ammonium.

2. Composition intumescente selon la revendication 1, comprenant de 5 à 95% en poids, sur la base du poids total du trioxa-2,6,7 phospho-1 bicyclo[2.2.2]octane méthanol-4 oxyde-1 et du composé azoté, de trioxa-2,6,7 phospho-1 bicyclo[2.2.2]octane méthanol-4 oxyde-1 et de 95% à 5% en poids, sur la base du poids total de trioxa-2,6,7 phospho-1 bicyclo[2.2.2]octane méthanol-4 oxyde-1 et du composé azoté, de composé azoté.

3. Articles formés préparés avec une composition intumescente comme revendiquée dans la revendication 1 ou 2.

4. Composition convenant à l'addition à une résine polymérique pour lui conférer de l'intumescence comprenant du trioxa-2,6,7 phospho-1 bicyclo[2.2.2]octane méthanol-4 oxyde-1 et un composé azoté qui est une mélamine, amméline, acide cyanurique, benzoguanamine, cyanamide, une urée ou une guanidine ou un de leurs sels ou un sel d'ammonium.

5. Composition selon la revendication 4, comprenant de 5 à 95% en poids, sur la base du poids total du trioxa-2,6,7 phospho-1 bicyclo[2.2.2]octane méthanol-4 oxyde-1 et du composé azoté, de trioxa-2,6,7-phospho-1 bicyclo[2.2.2]octane methanol-4 oxyde-1 et de 95% à 5% en poids, sur la base du poids total du trioxa-2,6,7 phospho-1 bicyclo[2.2.2]octane méthanol-4 oxyde-1 et du composé azoté, de composé azoté.